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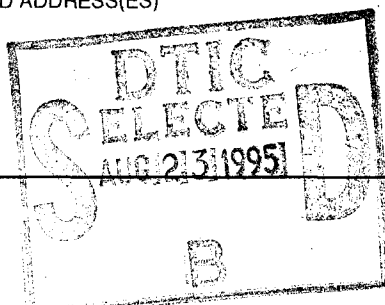
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The relationship between ultrahigh vacuum surface science and electrochemistry is examined by comparison of so-called non-situ and ex-situ experiments performed in the vacuum environment with in-situ electrochemical experiments. Preadsorbed ClO_4 on Ag (110) may be hydrated by post-adsorbed water and lifted off the surface as a hydrated complex at 170 K. This result directly illustrates the electrochemical concepts of anion desorption and nonspecific adsorption and can be explained by analogy to electrochemistry. For ex-situ studies three models exist to describe the key step of removing the electrode from the electrolyte (emersion): ideal, superequivalent, and dynamic. Ideal emersion obtains upon satisfying the criteria of (1) a 1:1 relationship of emersed work function with emersion potential and (2) zero charge transfer upon emersion. These criteria can be tested by Kelvin probe measurements of the work function in vacuum and re-immersion charge transient measurements in the electrochemical cell, respectively. Emersion of Pt(111) from 0.1 M HClO_4 + 1 mM Cu^{2+} exhibits ideal emersion at potentials greater than 0.7 V_{RHE} and superequivalent emersion, so called because superequivalent adsorption of ClO_4^- and Cl^- establishes a constant work function, at emersion potentials less than 0.6 V_{RHE} . The Pb/Pt(111) system exhibits dynamic emersion behavior, characterized by a surface redox reaction between Pb^0 and Pb^{2+} that discharges the double layer after emersion. Theoretical relationships among the non-situ, ex-situ, and in-situ methodologies are also briefly reviewed.

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by

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**RELATING THE IN-SITU, EX-SITU, AND NON-SITU
ENVIRONMENTS IN SURFACE ELECTROCHEMISTRY**

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ABSTRACT

The relationship between ultrahigh vacuum surface science and electrochemistry is examined by comparison of so-called non-situ and ex-situ experiments performed in the vacuum environment with in-situ electrochemical experiments. Preadsorbed ClO_4 on Ag (110) may be hydrated by post-adsorbed water and lifted off the surface as a hydrated complex at 170 K. This result directly illustrates the electrochemical concepts of anion desorption and nonspecific adsorption and can be explained by analogy to electrochemistry. For ex-situ studies three models exist to describe the key step of removing the electrode from the electrolyte (emersion): ideal, superequivalent, and dynamic. Ideal emersion obtains upon satisfying the criteria of (1) a 1:1 relationship of emersed work function with emersion potential and (2) zero charge transfer upon emersion. These criteria can be tested by Kelvin probe measurements of the work function in vacuum and re-immersion charge transient measurements in the electrochemical cell, respectively. Emersion of Pt(111) from 0.1 M HClO_4 + 1 mM Cu^{2+} exhibits ideal emersion at potentials greater than 0.7 V_{RHE} and superequivalent emersion, so called because superequivalent adsorption of ClO_4^- and Cl^- establishes a constant work function, at emersion potentials less than 0.6 V_{RHE} . The Pb/Pt(111) system exhibits dynamic emersion behavior, characterized by a surface redox reaction between Pb^0 and Pb^{2+} that discharges the double layer after emersion. Theoretical relationships among the non-situ, ex-situ, and in-situ methodologies are also briefly reviewed.

1. INTRODUCTION

Recent advances in in-situ instrumentation have brought about greatly improved characterization of electrode surfaces, but the question remains as to how to interpret these results within the context of surface science. The answer to this question requires both physical and conceptual links between electrochemistry and surface science. Theoretical studies provide the most appropriate conceptual link, yet both theoreticians and electrochemists need access to more fundamental experimental results. In this paper we illustrate through a number of examples how the ex-situ and non-situ experimental approaches can provide fundamental data that aid in understanding electrode surfaces.

1.1 Non-Situ Experiments

The most basic form of surface science experiment is the so-called non-situ experiment in which the electrode/electrolyte interface is simulated in ultrahigh vacuum (UHV) through adsorption of electrolyte species (solvent, ions, and neutral species) on a metal surface that serves as the model electrode. The term "non-situ" is meant simply to distinguish this experiment from the more well known in-situ and ex-situ measurements, while at the same time demonstrating the link between all three methods in a somewhat light-hearted way [1]. The rationale behind the non-situ approach (also known as double layer modeling) has been discussed at the conceptual, thermodynamic, and experimental levels by several authors [2-6]. The most appropriate model consists of adsorbed solvent and ionic species in sufficient quantities to establish a "bulk solution" phase at the electrode surface [5]. This takes the form of several multilayers of solvent, usually water, along with some form of coadsorbed electrolyte like HF, HCl, or HClO₄.

The link between electrochemical and vacuum simulations is manifested

through a common scale that relates potential in the electrochemical cell with work function in the vacuum chamber [2]. Figure 1 illustrates this relationship, which we refer to as the UHV-EC analogy, and includes several important features measured either in vacuum or the electrochemical cell. The precise alignment of the two scales depends upon the absolute potential E_k of the normal hydrogen electrode (NHE), a value ensconced in controversy, with estimates clustering around 4.4 V [7,8] or 4.8 V [9-11]. The important (and accepted) point is that such a value exists, and that work functions above E_k correspond to positive electrode potentials, whereas those below E_k correspond to negative electrode potentials. In fig. 1 E_k is set at the midpoint of the two values, 4.6 eV [12], and the uncertainty shown as an error bar of ± 0.2 eV. In addition, it is important to note that the electrochemical scale corresponds to a normal hydrogen electrode, for which hydronium ions in solution have unit activity; the potentials of hydrogen related reactions will shift with changes in hydronium ion activity. Thus, a complete comparison of UHV and EC scales requires knowledge of the effective pH of UHV grown adlayers, a topic that has not yet been addressed in non-situ studies.

Some of the most compelling experimental results that establish the UHV-EC analogy include the quantitative relationship between the C-O stretching frequency of adsorbed carbon monoxide and potential (whether electrochemical or vacuum) [6,12] and the findings of hydronium ion (H_3O^+) for coadsorbed H_2O and H on Pt(111) [13,14], Pt(100) [15], but not on Cu(110) [16]. The hydronium ion results can be readily understood in terms of the UHV-EC analogy. The 5.1 eV work function of Pt(111) with coadsorbed water and hydrogen corresponds to an electrochemical potential of 0.5 V_{NHE} , which is positive of the potential range where hydrogen adsorbs electrochemically on Pt(111) (see fig. 1). Thus, adsorbed hydrogen is not stable when the possibility exists for desorption into an aqueous phase. In the ultrahigh vacuum experiment desorption occurs by formation of

hydrated H_3O^+ in the water adlayer. In contrast to platinum, the work function of the water-covered copper surface is less than 4 eV, thus placing its effective electrode potential in a range where chemisorbed hydrogen is stable.

In view of this demonstration of cation desorption in the non-situ experiment, does the analogous case exist for non-situ anion desorption? According to the UHV-EC analogy, anion desorption would be favored by low electrode potentials, hence, low work functions, and an anion with a strong heat of hydration. We therefore chose as the model electrode Ag(110), which has a work function of 4.2 eV (3.6 eV with water [17]), and as the model anion ClO_4 , known to have only a weak tendency for specific adsorption [18]. The results described here will ascertain whether preadsorbed ClO_4 can be hydrated by water and lifted off the surface in a manner similar to anion desorption or nonspecific adsorption.

1.2 Ex-Situ (Emersion) Experiments

The ex-situ experiment involves removing an electrode from the electrolyte (a process called emersion) for subsequent analysis either in an ambient atmosphere or, more typically, an ultrahigh vacuum system. The most pressing questions here are: (1) How does the electrode change once it loses contact with the electrolyte? and (2) Given that some change is likely upon electrode removal, how can the emersed electrode be related to its in-situ state? The relevance of ex-situ experiments has been discussed on several occasions [20-26]. On the basis of a thermodynamic analysis of the emersion process [22,25,26], the following criteria for successful emersion can be defined:

- (1) The outer potential of the emersed electrode varies in a 1:1 relationship with emersion potential.

- (2) No charge transfer, either external or internal to the electrode, occurs upon emersion.

When emersion satisfies both criteria, the emersed adlayer accurately represents its emersed state. Strictly speaking, the outer potential of the emersed electrode should quantitatively follow the UHV-EC analogy; that is, it should agree with the emersion potential when converted with the proper value of E_k . This was recently tested by ex-situ measurements in which the electrode was emersed into a water-saturated, inert atmosphere [26]. Although both emersion criteria were met, the outer potentials differed from the expected values by an additive constant, the exact value of which depended on the nature of the electrolyte. The cause of this deviation was tentatively attributed to water restructuring in the emersed adlayer, though future study of this phenomenon is warranted. The ability to perform successful ex-situ studies (see, for example [11,19,23,24,27]) in spite of this problem of an additive constant demonstrates that the trends observed by ex-situ experiments are valid, but that absolute assessments of ex-situ results must be made with care.

The nature of emersion charge transfer is more significant, however, and is considered in some detail here. Figure 2 shows a schematic of an emersed electrode with a directly adsorbed layer and residual electrolyte. If the charged electrode were removed from the solution without its double layer, then an external emersion current i_{ex} would flow on account of the motion of a charged body. In practice, such currents do not flow, which verifies that the electrode emerges with its double layer as a neutral system [21,23]. However, the emersed electrode remains electrochemically active and an internal current i_{in} may flow if discharge of the double layer occurs. Such processes may be accompanied by exchange of (for example) hydrogen, carbon dioxide, or oxygen with the ambient gas. Although

internal charge transfer following emersion cannot be measured, its counterpart can, by measuring the charge transient upon re-immersing the electrode back into the electrolyte at the same potential. Re-immersion brings the electrode back to its in-situ state, thereby reversing the emersion discharge process, so that the re-immersion charge transient is equal and opposite in sign to the internal charge transfer of emersion. Combined measurements of the outer potential of the emersed electrode and its corresponding re-immersion charge transient therefore provide a full analysis of the emersion process for any system. In this paper we discuss several examples in which both, one, or none of the emersion criteria are fulfilled and define models for emersion that allow even non-ideally emersed electrodes to be related to their in-situ states.

2. EXPERIMENTAL PROCEDURE

The non-situ experiments were performed in a multi-technique ultrahigh vacuum chamber that has been described previously [15,28,29]. Characterization of the adsorbate was accomplished by thermal desorption spectroscopy (TDS), low energy electron diffraction, and high resolution electron energy loss spectroscopy (HREELS). The energy loss spectrometer (McAllister Technical Services) had a resolution of 100 cm^{-1} (full-width at half-maximum) and energy losses are reported to the nearest 5 cm^{-1} . The electron beam was incident upon the surface at an angle of 60° from the surface normal and only specularly scattered electrons were collected. The spectrometer was operated such that changes in sample bias required to attain the optimum spectrum reflect changes in sample work function. The position of the clean sample, biased at 0 V with respect to ground, was adjusted until the best spectrum was obtained without applied deflection of either incident or scattered electron beams. (For the McAllister spectrometer this corresponds to all ΔB potentials set to zero.) Subsequent changes in sample work function will deflect

both incident and scattered beams resulting in a weak or no energy loss spectrum unless the sample bias is adjusted to compensate for the change in work function. Following adsorption, then, only the sample bias was adjusted to obtain the optimum spectrum; an increase in sample bias corresponds to an increase in sample work function. The changes in sample bias and estimated work function changes are given in the figure caption. All energy loss spectra were recorded with the sample at 100 K after annealing to the indicated temperatures.

Nearly anhydrous HClO_4 dosing vapor was obtained from a solution of 70 wt % HClO_4 to which concentrated H_2SO_4 was added in a 1:1 ratio by volume [30]. The vapor was admitted to the vacuum chamber through a micro-capillary array doser [28] located within 5 mm of the sample, which was at 100 K. Adsorbed ClO_4 was prepared by exposing the $\text{Ag}(110)$ surface at 100 K to HClO_4 vapor followed by heating to 250 K to deprotonate the acid [30]. The $\text{Ag}(110)$ sample was prepared as described previously [28] and temperature was controlled over the range of 100-900 K.

The emersion experiments were performed in a system with combined ultrahigh vacuum and electrochemical capabilities [27]. Following emersion the electrode was either re-immersed back into the electrolyte at controlled potential or transferred to the vacuum chamber for measurement of its outer potential by a Kelvin probe (McAllister Technical Services). The outer potential of the reference electrode of the Kelvin probe was calibrated against a clean $\text{Pt}(111)$ surface in vacuum, for which the absolute work function is 5.94 ± 0.03 eV [31], and outer potentials of the emersed electrodes were converted to absolute work functions by comparison with the calibrated reference electrode. This calibration remained stable to within 50 mV over a period of six months.

Electrolytes were prepared from water treated by deionization, reverse

osmosis, and a Barnstead Nanopure water system. HClO_4 was doubly distilled and obtained from G.F. Smith Chemicals. The electrochemical cell employed a platinum foil counter electrode and gold|gold oxide reference electrode. Unless otherwise specified all potentials are reported against the reversible hydrogen electrode (RHE). Cyclic voltammograms were recorded with an EG&G 362 Potentiostat connected to a Hewlett-Packard 7090A digital/analog plotter. Re-immersion current transients were measured with the plotter in digital mode and graphically integrated to obtain the charge. The Pt(111) sample was prepared as previously described [27] and had a surface area of 0.6 cm^2 .

3. RESULTS AND DISCUSSION

3.1 Hydration of $\text{ClO}_4/\text{Ag}(110)$

High resolution electron energy loss spectra for approximately 0.1 monolayer of ClO_4 (one monolayer refers to the number of topmost silver atoms) adsorbed alone and fully hydrated are shown in fig. 3. For the nonhydrated case, curve (a), energy losses due to ClO_4 occur at 640, 910, 1020, and 1230 cm^{-1} . These are listed and compared with the Cl-O stretching frequencies of metal perchlorates and aqueous perchlorate ion in Table 1. The 1230 and 1020 cm^{-1} peaks, and the absence of a peak at $1100\text{-}1200 \text{ cm}^{-1}$ are in good agreement with tridentate perchlorate, that is, ClO_4 bonded to the surface through three oxygen atoms. Previously, we identified adsorbed perchlorate as bidentate on the basis of two lobes of O^+ emission in the electron simulated desorption ion angular distribution (ESDIAD) [30]. However, the ESDIAD result can be equally well described by a model of tridentate adsorption in which the bond between chlorine and the oxygen not in contact with the surface is tilted away from the surface normal [35].

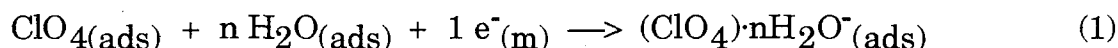
The remaining peaks in fig. 3(a) can be assigned as follows. The peak near 2400 cm^{-1} is an overtone of the 1230 cm^{-1} peak. The peaks at 3000 and 3560 cm^{-1}

represent, respectively, the O-H stretches of strongly and weakly hydrogen bonded water [36]. This water, which amounts to less than 0.04 monolayer as measured by TDS, arises from residual water in the perchloric acid dosing vapor and adsorption from the background gas in the vacuum chamber. The low value of 3000 cm^{-1} for an O-H stretch may represent water molecules with one hydrogen pointing to the surface on account of the other hydrogen interacting with ClO_4 . Similarly low values have been observed for water interacting with alkali atoms on copper [37] and platinum [38] surfaces. The 3560 cm^{-1} peak would therefore represent the O-H stretch of the $\text{O-H}\cdots\text{OClO}_3$ moiety, although a more definitive study is required for a definitive assignment.

The energy loss spectrum changes completely upon hydration of the ClO_4 adlayer, as shown in fig. 3(b). For this spectrum sufficient water was adsorbed for complete hydration of perchlorate and excess multilayer water was removed by annealing the sample to 170 K. Subsequent thermal desorption analysis showed that the hydrating water desorbed in a single peak at 182 K and that the $\text{H}_2\text{O}:\text{ClO}_4$ ratio was $5\pm 1:1$. The hydrating water is evident in the energy loss spectrum by frustrated translations at 200 cm^{-1} , librational modes at 735 cm^{-1} , the scissoring mode at 1660 cm^{-1} , and O-H stretching modes at 3000 cm^{-1} (weak) and 3560 cm^{-1} (intense). Only the peak at 1090 cm^{-1} can be assigned to the ClO_4 species (Table 1). This peak represents the asymmetric Cl-O stretch shifted to lower energy from the 1230 cm^{-1} peak in fig. 3(a) and is in excellent agreement with the asymmetric Cl-O stretch of tetrahedral ClO_4^- . This assignment is further supported by the absence of peaks in the range of $1150\text{-}1300\text{ cm}^{-1}$, which would appear for lower symmetries of perchlorate.

The changes in the energy losses for perchlorate between (a) and (b) of fig. 3 bear a strong similarity with in-situ infrared data of Pt(111) in perchloric acid electrolyte for which a strong band at 1119 cm^{-1} was attributed to ClO_4^- in solution

and a band at 1218-1234 cm^{-1} was attributed to tridentate ClO_4 adsorbed directly on the electrode [39]. The change in perchlorate adsorption upon hydration can be similarly interpreted in terms of a change of symmetry from C_{3v} or lower for the unhydrated molecule to the highly symmetric T_d (tetrahedral) form for the fully hydrated molecule. Since bonding to the substrate causes the reduction in symmetry for the nonhydrated case, the high symmetry of hydrated perchlorate is evidence for the absence of direct interaction between ClO_4 and the substrate. The process of perchlorate hydration may be depicted as



in which the subscript m signifies that the electronic charge comes from the metal and the product is a fully hydrated perchlorate ion without direct contact to the surface. This, formally, is a description of a nonspecifically adsorbed anion, analogous to the case in electrochemistry, but here isolated in a non-situ experiment. The thermodynamic feasibility of eq. (1) has been analyzed in terms of a Born-Haber cycle [35].

The data presented here allow a qualitative, but unfortunately not quantitative, test of the UHV-EC analogy. The estimated work function change of fully hydrated ClO_4 on Ag(110) corresponds to an absolute work function of 4.3 eV and an electrochemical potential approximately 0.4 V positive of the potential of zero charge (PZC) [18]. At the PZC the level of specific adsorption of ClO_4^- is weaker than that of F^- , but stronger than that of PF_6^- ; the coverage of perchlorate varies between effectively zero to approximately 0.01 monolayer for electrolyte concentrations ranging from 0.01 to 0.1 M [18]. More positive potentials will lead to increased specific adsorption of perchlorate ion, but to our knowledge the in-situ

adsorption isotherm for ClO_4^- on Ag(110) has not been reported. Thus, we cannot quantitatively compare the in-situ and non-situ results because the equivalent coverage of specifically adsorbed perchlorate in-situ cannot be estimated and because the bulk concentration of perchlorate cannot be defined for this non-situ experiment. The latter problem points to the necessity of having a properly defined "bulk" phase in the non-situ experiment (as was done in the hydronium ion/Pt(100) study [15]), which we will attempt for this system in future experiments. Nonetheless, the qualitative aspects of the UHV-EC analogy remain valid, namely, that combination of a low work function substrate with a weakly specifically adsorbing anion in a non-situ experiment successfully models the concept of nonspecific adsorption in the in-situ environment. This result complements that for H_3O^+ on a high work function surface, for which the UHV-EC analogy has been examined in a more quantitative fashion [2,15].

3.2 Emersion Studies

The basic set of data needed to evaluate an emersion experiment is shown in fig. 4. for emersion of Pt(111) from 0.1 M HClO_4 with 1 mM Cu^{2+} in solution. The cyclic voltammogram (a) shows the multilayer and monolayer stripping peaks for copper at 0.31 and 0.7 V, respectively, and agrees with earlier studies [23,40-43]. The re-immersion charge transient curve (b) shows, in the direction of positive to negative potentials, small anodic charge transfer at potentials above 0.25 V, zero charge transfer at 0.25 V, and significant cathodic charge transfer at lower potentials. The emersed work function curve (c) shows a 1 eV/V shift with emersion potential down to 0.7 V, a discontinuity in the region of 0.55 - 0.7 V, and a constant, high work function at lower potentials to about 0.05 V.

The re-immersion charge transient curve allows both quantitative and qualitative estimates of the change in electrode potential brought about by post-

emersion processes. The emersed potential, defined as the electrode potential after contact with the electrolyte is lost, will approach the zero-crossing potential (0.25 V) by discharge through an oxidative or reductive process. The extent to which this occurs is given by the magnitude of the re-immersion charge transient. At an emersion potential of 0.6 V, for which the positive sweep of the cyclic voltammogram (a) may be characterized by a capacitance of $140 \mu\text{F}/\text{cm}^2$, the charge transient of $2 \mu\text{C}/\text{cm}^2$ corresponds to a change in potential of just -14 mV, truly a small amount. At more positive emersion potentials the monolayer copper stripping peak provides a buffer against changes in potential after emersion; small charge transients may be accommodated by adsorption or desorption of copper. Thus, a re-immersion charge transient of $5 \mu\text{C}/\text{cm}^2$ (corresponding to $-5 \mu\text{C}/\text{cm}^2$ upon emersion) can be satisfied by adsorption of 0.01 monolayers of Cu^{2+} .

A more qualitative estimate of emersion charge transfer may be obtained by comparing the slope of the charge transient curve, which represents an emersion capacitance, with a characteristic capacitance of the system, in this case the value of $140 \mu\text{F}/\text{cm}^2$ obtained from the voltammogram. In the region above 0.25 V the slope of the charge transient curve is $8 \mu\text{F}/\text{cm}^2$, or just 6% of the characteristic capacitance, so the emersed charge transfer is small for emersion potentials above 0.25 V.

While the criterion of no emersion charge transfer is satisfied over nearly the entire potential range studied, the 1:1 variation of work function with emersion potential was obeyed only over a limited potential range. Thus, "ideal" emersion occurs only for emersion potentials above 0.7 V. As has been done previously [11], the emersed work function curve may be extrapolated to 0 V to obtain an estimate of the absolute electrode potential. The extrapolated value of 4.95 eV corresponds to a value of 5.01 eV when adjusted to the normal hydrogen electrode scale. This is 0.2 eV higher than the upper range of previously reported values [9-11] and may arise

from a discrepancy by an additive constant as mentioned above.

For emersion potentials less than 0.6 V, ex-situ Auger data, shown in fig. 5, indicated that anions from the bulk electrolyte adsorb along with copper. Similar results have been obtained in previous studies [41-46]. The Auger signals for Cu, Cl, and O all increase steadily with decreasing potential indicating that adsorption of ClO_4^- (and possibly Cl^- present as an impurity) is proportional to the amount of adsorbed copper. Apparently, the uptake of ions causes the emersed work function to remain constant for as yet unknown reasons. Only one of the criteria for ideal emersion is satisfied in this case (zero charge transfer) so we identify this emersion model as superequivalent emersion in view of the influence of superequivalent ion adsorption on the emersed work function.

The situation where both criteria of ideal emersion are unsatisfied is exhibited by the Pb/Pt(111) system, which has been previously described [27]. Figure 6 shows the set of re-immersion data for this system. The cyclic voltammogram (a) is in good agreement with previous work [27,47,48] and the set of peaks at 0.65 V corresponds to the surface redox reaction between adsorbed Pb^0 and Pb^{2+} . Note that the re-immersion charge transient curve (b) exhibits very large magnitudes at the two potential limits and crosses zero at the same potential as the surface redox peak in curve (a). This emersion system has been labeled dynamic emersion in view of the $\text{Pb}^0/\text{Pb}^{2+}$ surface redox reaction, which causes discharge of the emersed adlayer until a new equilibrium between Pb^0 and Pb^{2+} is established. The resulting emersed potential E_{em} can be estimated from a Nernst equation written for the surface redox reaction

$$E_{em} = E^0 - \frac{RT}{2F} \ln(n^0 / n^{2+}) \quad (2)$$

where E^o is the standard reduction potential (0.65 V) and n^0 and n^{2+} the coverages of Pb^0 and Pb^{2+} as measured by x-ray photoelectron spectroscopy (XPS). From the ex-situ XPS results [27], the emersed potential can vary only by 40 mV in the range of 0.62 - 0.66 V. This finding therefore predicts a constant emersed work function over the entire potential range, which is confirmed by the data of fig. 6(c). The 40 mV range of emersed potential falls within the standard deviation of the work function measurements. In this case of dynamic emersion the emersed adlayer experiences near or total discharge, but the relative amounts of Pb^0 , Pb^{2+} and coadsorbed ions retain information about the in-situ environment [27].

4. SUMMARY AND CONCLUSIONS

Non-situ and ex-situ studies can provide important information for understanding the electrode/electrolyte interface. The ability of water to hydrate preadsorbed ClO_4^- and lift it off the Ag(110) surface illustrates the concepts of anion desorption and nonspecific adsorption in a manner readily identifiable with traditional electrochemical concepts. Furthermore, this strictly UHV behavior follows, qualitatively at least, the UHV-EC analogy. Consideration of both the $ClO_4^-/Ag(110)$ system and its cationic counterpart of H_3O^+/Pt verifies that the UHV-EC analogy has broad applicability and is not limited to any special case.

The three emersion models; ideal, superequivalent, and dynamic; cover all known classes of emersion. They apply when respectively both, one, or none of the emersion criteria are fulfilled. Although ideal emersion may prove the exception rather than the rule, there is no doubt that a suitably well controlled emersed adlayer represents the state of the in-situ system in some way. By classifying emersion into a series of models, we can elucidate exactly what kinds of in-situ information, and under what conditions, are accessible to ex-situ experiments. In so

doing the uncertainty associated with the emersion process is lifted, thereby establishing the general applicability of this method for fundamental studies of electrochemistry.

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REFERENCES

1. M. J. Weaver and X. Gao, *Ann. Rev. Phys. Chem.* 44 (1993) 459.
2. J. K. Sass, D. Lackey, J. Schott, and B. Staehler, *Surf. Sci.* 247 (1991) 239.
3. G. Pirug and H. P. Bonzel, in Structure of Electrified Interfaces, J. Lipkowski and P. N. Ross (Eds.) (VCH Publishers, New York, 1992) p. 153.
4. F. T. Wagner, in Structure of Electrified Interfaces, J. Lipkowski and P. N. Ross (Eds.) (VCH Publishers, New York, 1992) p. 309.
5. E. M. Stuve and N. Kizhakevariam, *J. Vac. Sci. Tech. A* 11 (1993) 2217.
6. I. Villegas, N. Kizhakevariam, and M. J. Weaver, this volume.
7. S. Trasatti, *Pure Appl. Chem.* 58 (1986) 955.
8. W. N. Hansen and G. J. Hansen, *Phys. Rev. A* 36 (1987) 1396.
9. R. Gomer and G. Tryson, *J. Chem. Phys.* 66 (1977) 4413.
10. W. N. Hansen and D. M. Kolb, *J. Electroanal. Chem.* 100 (1979) 493.
11. E. R. Kötz, H. Neff, and K. Müller, *J. Electroanal. Chem.* 215 (1986) 331.

12. S.-C. Chang and M. J. Weaver, *J. Phys. Chem.* 95 (1991) 5391.
13. F. T. Wagner and T. E. Moylan, *Surf. Sci.* 206 (1988) 187.
14. D. Lackey, J. Schott, J. K. Sass, S. I. Woo, and F. T. Wagner, *Chem. Phys. Lett.* 184 (1991) 277.
15. N. Kizhakevariam and E. M. Stuve, *Surf. Sci.* 275 (1992) 223.
16. D. Lackey, J. Schott, and J. K. Sass, *J. Electron. Spec. Rel. Phenom.* 54/55 (1990) 649.
17. K. Bange, T. E. Madey, J. K. Sass, and E. M. Stuve, *Surf. Sci.* 183 (1987) 334.
18. G. Valette, *J. Electroanal. Chem.* 122 (1981) 285.
19. P. N. Ross and F. T. Wagner, in *Adv. Electrochem. and Electrochem. Eng.*, Vol. 13, H. Gerischer and C. W. Tobias (Eds.) (Wiley-Interscience, New York, 1984).
20. P. M. A. Sherwood, *Chem. Soc. Rev.* 14 (1985) 1.
21. W. N. Hansen, *J. Electroanal. Chem.* 150 (1986) 133.
22. D. Aberdam, R. Durand, R. Faure, and F. El-Omar, *Surf. Sci.* 171 (1986) 303.
23. D. M. Kolb, *Z. Phys. Chem. N. F.* 154 (1987) 179.
24. A. T. Hubbard, *Chem. Rev.* 88 (1988) 633.
25. E. M. Stuve, R. L. Borup, and D. E. Sauer, in The Application of Surface Analysis Methods to Environmental/Material Interactions, PV 91-7, D. R. Baer, C. D. Clayton, and G. D. Davis (Eds.) (Electrochem. Soc., Pennington, New Jersey, 1991).
26. Z. Samec, B. W. Johnson, and K. Doblhofer, *Surf. Sci.* 264 (1992) 440.
27. R. L. Borup, D. E. Sauer, and E. M. Stuve, *Surf. Sci.* 293 (1993) 10; 27.
28. R. Döhl-Oelze, C. C. Brown, S. Stark, and E. M. Stuve, *Surf. Sci.* 210 (1989) 339.
29. A. Krasnopoler and E. M. Stuve, submitted to *Surf. Sci.*
30. N. Kizhakevariam, R. Döhl-Oelze, and E. M. Stuve, *J. Phys. Chem.* 94 (1990) 5934.

31. H. H. Rotermund, S. Jakubith, A. von Oertzen, and G. Ertl, *J. Chem. Phys.* 91 (1989) 4942.
32. F. Favier and J.-L. Pascal, *J. Chem. Soc. Dalton Trans.* (1992) 1997.
33. B. J. Hathaway and A. E. Underhill, *J. Chem. Soc. London* (1961) 3091.
34. G. Herzberg, Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra, (Van Nostrand Reinhold, New York, 1945) p. 167.
35. A. Krasnopoler and E. M. Stuve, in preparation.
36. R. Brosseau, M. R. Brustein, and T. H. Ellis, *Surf. Sci.* 280 (1993) 23.
37. D. Lackey, J. Schott, B. Straehler, and J. K. Sass, *J. Chem. Phys.* 91 (1989) 1365.
38. P. Baumann, G. Pirug, D. Reuter, and H. P. Bonzel, this volume.
39. Y. Sawatari, J. Inukai, and M. Ito, *J. Electron. Spec. Relat. Phenom.* 64/65 (1993) 515.
40. J. Stickney, S. Rosasco, and A. T. Hubbard, *J. Electrochem. Soc.* 131 (1984) 260.
41. L.-W. H. Leung, T. W. Gregg, and D. W. Goodman, *Langmuir* 7 (1991) 3205.
42. K. Sashikata, N. Furuya, and K. Itaya, *J. Electroanal. Chem.* 316 (1991) 361.
43. N. Markovic and P. N. Ross, *Langmuir* 9 (1993) 580.
44. N. Markovic, I. M. Tidswell, C. A. Lucas, and P. N. Ross, this volume.
45. H. A. Abruña, this volume.
46. M. Ito, this volume.
47. J. Clavilier, J. M. Orts, J. M. Feliu, and A. Aldaz, *J. Electroanal. Chem.* 193 (1990) 197.
48. R. R. Adzic, J. Wang, C. M. Vitus, and B. M. Ocko, *Surf. Sci. Lett.* 293 (1993) L876.

Table 1.
Cl-O Stretching Frequencies (cm^{-1}) for $\text{ClO}_4/\text{Ag}(110)$,
 ClO_4^- in solution, and selected metal perchlorates.

Mode	ClO_4^-/Ag fig. 3(a)	$\text{M}(\text{ClO}_4)_3^{\text{a}}$ C_{3v} tridentate	$\text{Cu}(\text{ClO}_4)_2$ C_{2v} bidentate	$\text{Cu}(\text{ClO}_4)_2^{\text{b}}$ C_{3v} monodentate	ClO_4^- T_d tetrahedral	$\text{H}_2\text{O}/\text{ClO}_4^-/\text{Ag}$ fig. 3(b)
ν_a	1230	1250-1267	1245-1270	1158	—	—
ν_a	—	—	1130	—	1110	1090
ν_a	1020	1000-1100	1030	1030	—	—
ν_s	915	920	920,948	920	932 ^c	—
Ref.	—	[32]	[33]	[33]	[34]	—

a) $\text{M} = \text{Y, La, Nd, Sm, Gd, Er}$.

b) Dihydrate form.

c) Infrared inactive.

FIGURE CAPTIONS

Figure 1: The UHV-EC analogy, as illustrated by comparison of the electrode potential and vacuum work function scales. All silver data are for Ag(110) and all platinum data are for Pt(111). See text for details. Adapted from [2].

Figure 2: Schematic of an emersed electrode with an adsorbed layer and a layer of residual electrolyte. Emersion may cause an external current flow i_{ex} and post-emersion relaxation of the double layer may result in an internal current flow i_{in} .

Figure 3: Ion energy loss spectra for approximately 0.1 monolayer of ClO_4 adsorbed on Pt(110) in the nonhydrated (a) and fully hydrated (b) states. Following adsorption for (b), the sample was heated to 170 K to remove multilayer water. The change in sample bias (from the clean surface) was +1.9 V and +0.1 V for (a) and (b) respectively. This change in bias corresponds approximately to the work function change from the clean surface (see text).

Figure 4: Selected emersion data for Pt(111) in 0.1 M HClO_4 + 1 mM Cu^{2+} : (a) cyclic voltammogram recorded at 50 mV/s; (b) re-immersion charge transient; and (c) emersed work function measured after transfer to UHV.

Figure 5: Relative coverages, measured by ex-situ Auger spectroscopy, of Cu, Cl, and O on Pt(111) corresponding to the conditions of fig. 4(c). The ordinate shows the peak-to-peak Auger ratio for Cu, Cl, and O relative to that of Pt.

Figure 6: The same as fig. 4, except for emersion from 0.1 M HClO_4 + 1 mM Pb^{2+} .

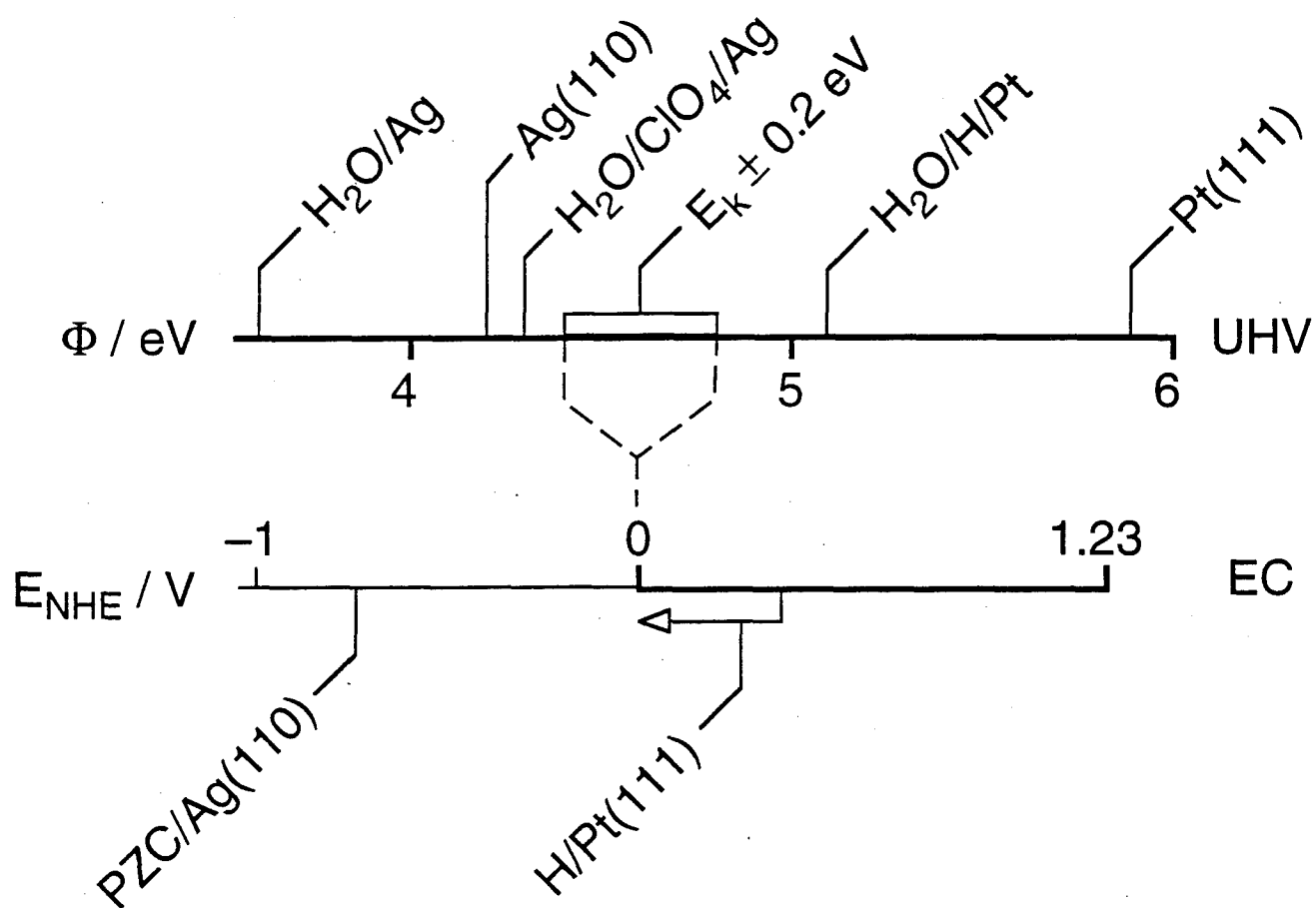


Fig. 1, Stuve et al.

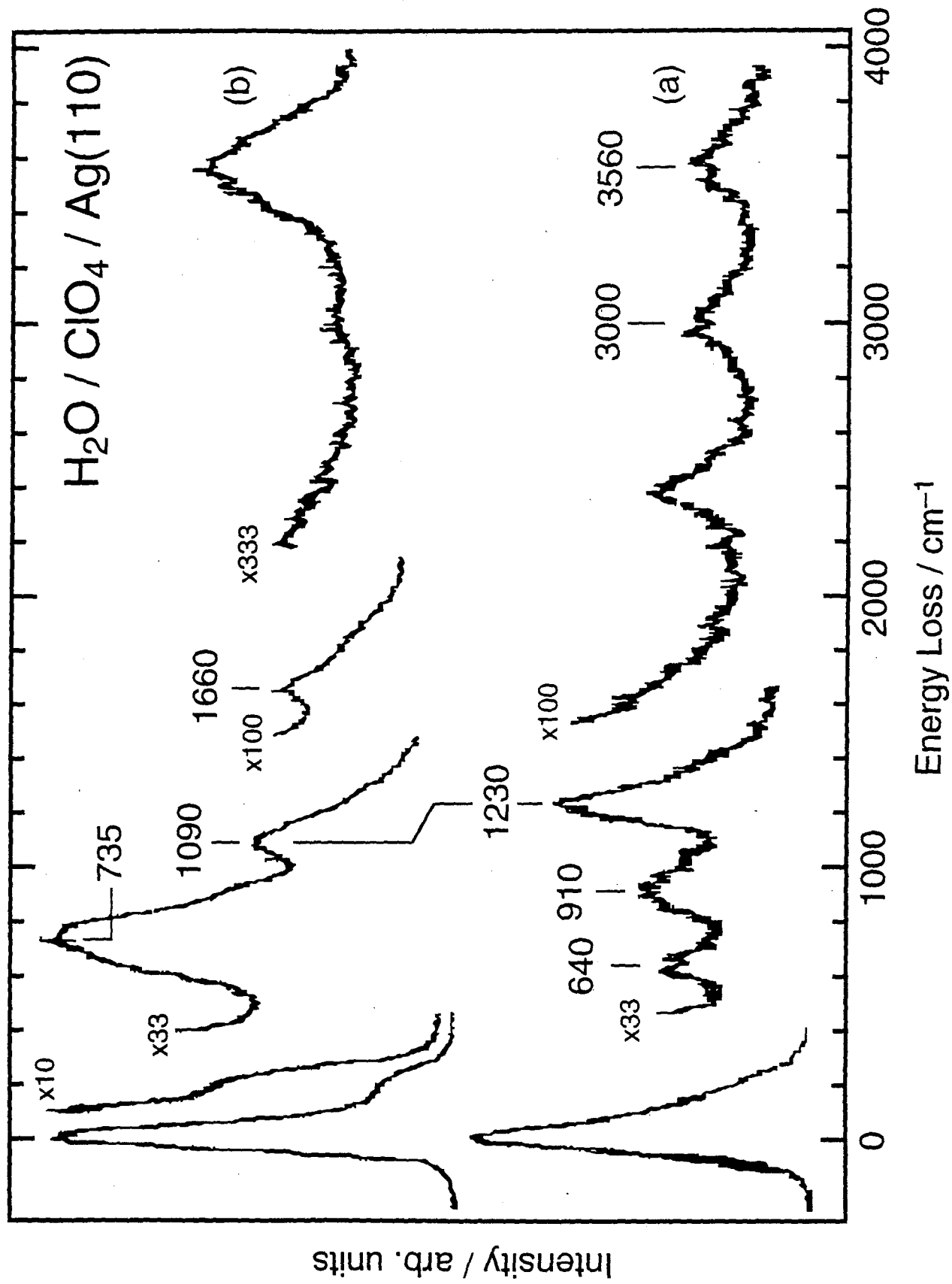


Fig. 3, Stuve et al.

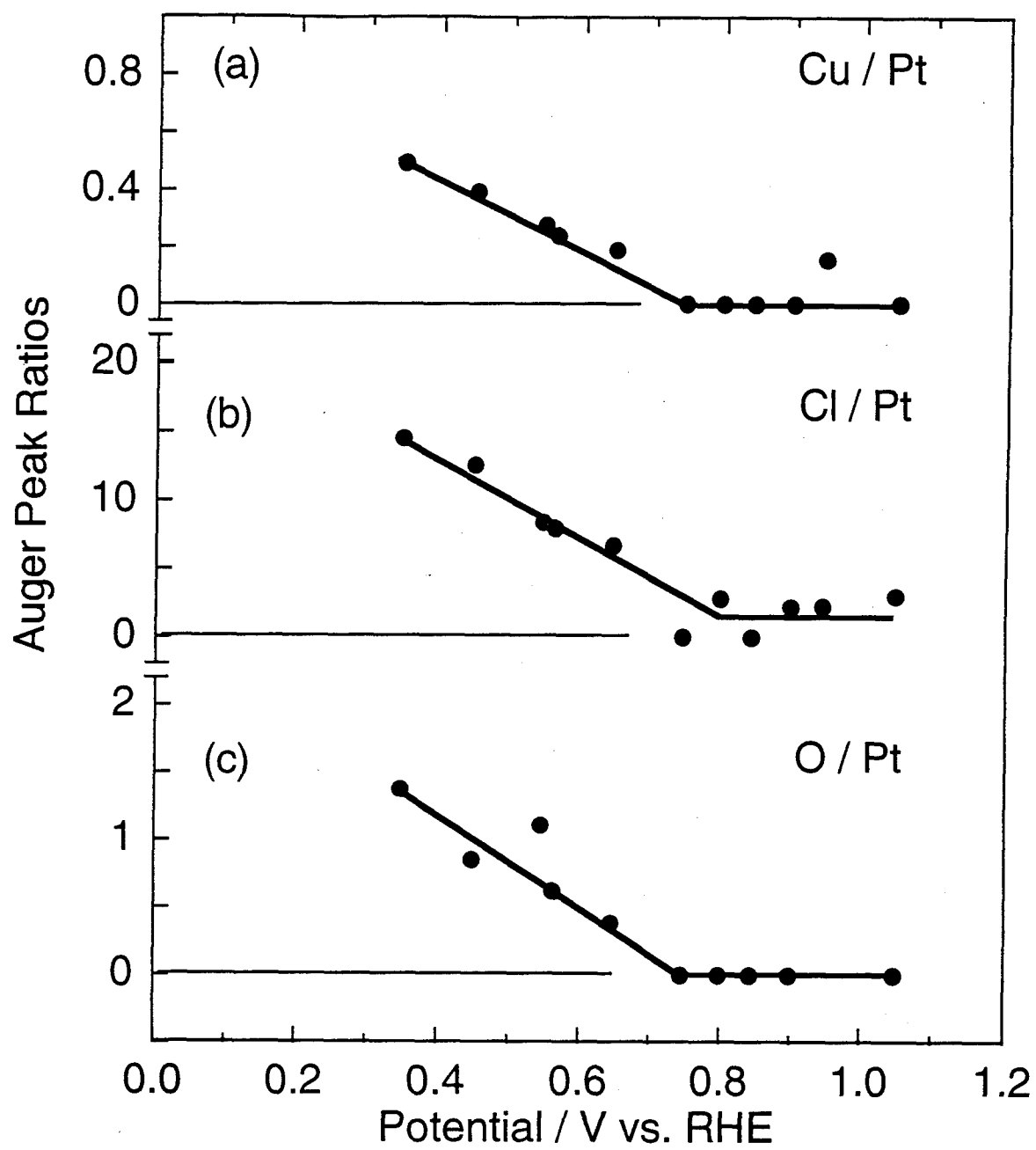


Fig. 5, Stuve et al.